

Laboratory Name: Savannah River National Lab
B&R Code: KC020103

FWP and possible subtask under FWP:

Elucidation of Hydrogen Interaction Mechanisms with Metal-Doped Carbon Nanostructures

FWP Number:

SCW-0024

Program Scope:

This research work is aimed at obtaining a better understanding of the nanoscale level of hydrogen sorption behavior of Metal-Doped Carbon Nanostructures. The experimental work is closely linked to relevant modeling studies of these materials. Advances in hydrogen storage technology based on carbon nanostructures and particularly metal-doped carbon nanotube (MD-CNT) require the development of a basic understanding of their physicochemical properties and the manner in which these properties influence the hydrogen bonding. Our effort is focused on understanding of the hydrogen interaction mechanisms such as physisorption, weak covalent bonding, and chemisorption in these nano-carbon systems.

Major Program Achievements (over duration of support):

Carbon nanotubes doped with different metals have been produced and the process is being optimized. The ultimate goal is to control the size and type as needed. Different diameter batches of carbon nanotubes were produced in order to investigate the effect of curvature on the hydrogen bond.

Recent studies illustrate that metallization of carbon nanotubes and fullerenes may enhance the strength of hydrogen bonding and lead to high gravimetric density. However, choosing the correct metal dopant is essential as they may cluster on the carbon frame and adversely affect the hydrogen gravimetric density. Using density functional theory we show that Li coated C₆₀ fullerene may be a potential candidate for hydrogen storage. In particular, Li₁₂C₆₀ with the Li atoms located on the 12 pentagonal faces of the fullerene is able to store 120 hydrogen atoms in molecular form yielding a gravimetric density of 13 wt % and a volumetric density of 128 g/L.

Program impact:

Provides insight into likely metal-carbon structures for hydrogen storage materials.

Interactions:

Internal: Weekly progress meetings, technical meetings as needed

External: Clemson University, University of South Carolina Aiken, Virginia Commonwealth University

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

none

Personnel Commitments for FY2005 to Nearest +/- 10%:

Ragaiy Zidan 25%

Polly Berseth (post-doc) 50%

Steve Serkiz 5%

Scott McWhorter 20%

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FWP and possible subtask under FWP:

Mechanistic Aspects of the Formation and Decomposition of Transition Metal Doped Complex Hydrides (this project is a continuation of SCW-0024 "Elucidation of Hydrogen Interaction Mechanisms with Metal-Doped Carbon Nanostructures")

FWP Number:

SCW-0024

Program Scope:

The program involves investigating the thermodynamics governing formation of complex metal hydrides via mechanosynthetic techniques. Both ball milling and molten state processing techniques have been employed on a series of metal hydride and complex metal hydride reagents in order to synthesize $M(AlH_4)_x$ and $M_xM'_{3-x}AlH_6$ species. Further, the role of catalysts in the synthetic process has been examined. Novel materials will be investigated by vibrational spectroscopy including inelastic neutron scattering (INS) to investigate the phonon vibrations and the effect of the catalyst on the local lattice structure.

Major Program Achievements (over duration of support):

It was determined that the molten state process of synthesizing complex metal hydride materials is largely governed by thermodynamic stability. A series of complex aluminum hydrides have been combined with alkali hydrides or other complex aluminum hydrides under hydrogen pressure and high temperatures such that the most thermodynamically stable product will be observed at the end of the reaction. When however, a salt side product can be formed which will drive the free energy of the reaction, complex metal hydrides result which by themselves are thermodynamically unstable. These materials—for example $Mg(AlH_4)_2$ —are kinetically hindered toward decomposition. Thermodynamic calculations have also been used to compliment the experimental work. A series of $NaAlH_4$ and Ti-doped $NaAlH_4$ have been investigated by vibrational spectroscopy in order to gain insight into the role of Ti in catalyzing reversible H_2 release. INS has been employed at low temperatures since the technique is unbiased toward the origin and nature of molecular vibrations to investigate subtle changes to the lattice of $NaAlH_4$ as a function of mechanical milling time and doping level. Ti-doping of the material alters the lattice structure locally although the average crystal structure (obtained via powder XRD) remains the same. This subtle change may lead to the observed reversible H_2 sorption.

Program impact:

With an understanding of the molten state process, synthesis of novel complex metal hydride materials can be better planned. When thermodynamically unstable materials are desired, reagents which will result in side products with favorable thermodynamic quantities can be used to drive the synthesis toward unstable materials. Potential hydrogen storage materials can be prepared for the first time. The employment of neutron scattering to these materials provides access to molecular interactions in the lattice which are presumed to be integral to the dehydrogenation process. Better materials can be engineered when the role of Ti-doping understood.

Interactions:

Internal: technical meetings

Extrenal: lecture at Southeastern region Meeting of the ACS, lecture at the International Symposium on Metal-Hydrogen Systems 2006

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

none

Personnel Commitments for FY2005 to Nearest +/- 10%:

Ragaiy Zidan 25%

Don Anton 10%

Ashley Stowe (post-doc) 50%

Thomas Farrell (summer intern; Furman University undergraduate student) 3%

Laura Laughlin (summer intern; Clemson University undergraduate student) 2%

Authorized Combined Budget (BA) for FY04, FY05, FY06:

FY04 BA \$-0-

FY05 BA \$200K

FY06 BA \$300K